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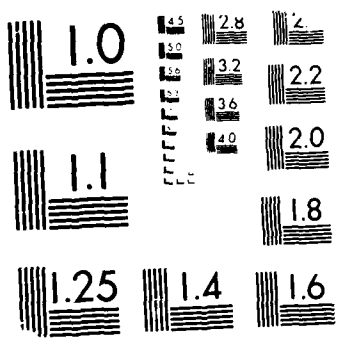

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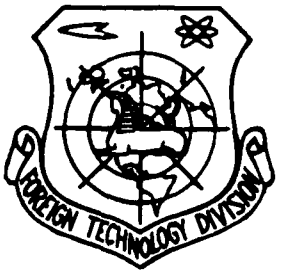
by

I. Yu. Mukhina, M.A. Timonova, et al.



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О о	*О о*	O, o	Ю ю	*Ю ю*	Yu, yu
П п	*П п*	P, p	Я я	*Я я*	Ya, ya

*ye initially, after vowels, and after ъ, ь; e elsewhere.
When written as ё in Russian, transliterate as yё or ё.

RUSSIAN AND ENGLISH TRIGONOMETRIC FUNCTIONS

Russian	English	Russian	English	Russian	English
sin	sin	sh	sinh	arc sh	$\sinh^{-1}$
cos	cos	ch	cosh	arc ch	$\cosh^{-1}$
tg	tan	th	tanh	arc th	$\tanh^{-1}$
ctg	cot	cth	coth	arc cth	$\coth^{-1}$
sec	sec	sch	sech	arc sch	sech^{-1}
cosec	csc	csch	csch	arc csch	csch^{-1}

Russian	English
rot	curl
lg	log

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CORROSION AND ELECTROCHEMICAL BEHAVIOR OF BINARY MAGNESIUM ALLOYS

I. Yu. Mukhina, M. A. Timonova, M. B. Al'tman, T. I. Yershova

Abstract

A systematic investigation of the effect of 23 elements on the corrosion behavior of magnesium alloys in a 3% solution of NaCl and in a humid atmosphere was carried out. The values of the stationary potentials and the variation of the potentials through time are determined.

The purpose of this work is to make a systematic investigation of the effect of alloying additives on the corrosion resistance and electrochemical characteristics of magnesium alloys. It is very interesting to study the corrosion behavior of binary systems, not only from the theoretical standpoint, but also from the practical one, since the selection of systems for developing corrosion-resistant alloys would be essentially random without these data.

Reports [1-5] give data about the effect of some elements on the corrosion and electrochemical behavior of magnesium alloys. However,

the information in the literature about the systematic investigation of the effect of alloying components on the corrosion characteristics of magnesium alloys is inadequate. In certain cases, the published data are contradictory, since uncontrolled impurities were present in the alloys along with the alloying additives. The tests were conducted in different media and it would be inaccurate to compare the findings with each other.

Investigation Procedure

When conducting the work, the authors attempted to eliminate the effect of impurities and technological factors in order to reveal the effect of the alloying components.

The alloys were prepared in a molybdenum crucible in order to keep the melt from being saturated with iron [6-8]. The purest possible source materials were selected. Sublimated high-purity magnesium with the following impurity content (in %) was used for melting: 0.002 Fe; 0.001 Cu; <0.0005 Ni; 0.001 Si; 0.002 Mn, 0.001 Pb. We know that the presence of impurities greatly reduces the corrosion resistance of magnesium alloys [1, 9, 10]. Therefore, the content of iron, copper, nickel and chloride-ion impurities was monitored. The samples were cast in a cast iron mold preliminarily painted with special paint and heated to 200°C. Volatile components with high, moderate and low solubility in magnesium (see the table) were used to obtain homogeneous and heterogeneous alloys.

Table. Solubility of components in magnesium alloys (according to data of G. V. Reynor et al).

(1) Группа элементов	(2) Компонент	Растворимость в магниевых сплавах % вес. (3)		(6) Содержание легирующего компонента в сплавах % вес
		(4) максимальная	(5) при 20°	
IA	Li	5,52	5,52	0,45; 4,80; 8,50; 11,0
IB	Cu	0,55	—	0,48; 2,81; 5,00
	Ag	16,0	—	0,64; 1,12
IIA	Ca	1,8	—	0,1; 0,37; 0,76; 2,80; 5,70
IIB	Zn	8,4	1,5	0,4; 3,30; 5,00
	Cd	100	100	0,73; 4,41
IIIA	Sc	32,0—34,0	(7) 15,0	0,31; 1,00; 2,55; 16,0
	La	1,9	Незначительная	1,00; 5,00
	Ce	1,6—0,74	»	0,35; 6,70
	Pr		»	0,61; 5,70
	Nd	2,0—3,6	0,8—1,0	0,59; 5,68
IIIB	Al	12,7	2,0	0,55; 1,11; 4,80
	Ga	8,6	—	0,78; 3,48; 5,48
	In	53,2	45,2	0,53; 4,85
	Tl	60,5	39,8	0,50; 5,00; 7,8
	Zr	0,8	0,2	0,20; 0,41; 0,61
IVB	Si	0,12	—	0,54; 1,30; 3,74
	Sn	15,33	0,1	0,50; 3,55; 5,00
	Pb	41,7	4,1	0,34; 4,80; 7,00
VB	Sb	0,1	—	0,067; 1,00
	Bi	11,4	—	1,00; 5,82; 8,16
VIIA	Mn	3,4	—	0,75; 1,06; 2,95

NOTE: The investigated alloys had the following impurity contents: Fe $\leq$0.003; [?] <0.0005%; Cu <0.003; exceptions: Mg-Ca, Fe=0.007%; Mg-Sc, Fe=0.02%; Mg-Ce, Fe=0.008%.

KEY: (1) Group of elements. (2) Component. (3) Solubility in magnesium alloys, % by weight. (4) Maximum. (5) At 20°. (6) Content of alloying component in alloys, % by weight. (7) Insignificant.

Magnesium alloys of 23 binary systems (see the table) were investigated. The effect of iron and nickel as alloying additives was not studied, since there is a large quantity of unambiguous data

which indicate a significant reduction in the corrosion resistance of alloys when these elements are present [1, 9, 10, etc.].

The corrosion tests were conducted in a 3% solution of NaCl and in a humid atmosphere above fresh water. The corrosion resistance of the alloys was estimated from the amount of hydrogen liberated per unit surface area and the change in the weight of the specimen. Potentiometer R-300 was used for the electrochemical investigations. The potentials of the substances through time were measured continuously for 48 hours. The steady-state value of the potential after six hours was used when discussing the results.

Results of Experiments and Discussion

The results of the effect of alloying on the corrosion rate of magnesium alloys in a 3% solution of NaCl and in a humid atmosphere are shown in Fig. 1. It should be noted that the laws governing the effect of alloying components on the corrosion rate in a 3% solution of NaCl are not always true for the conditions of a humid atmosphere because of differences in the kinetics of the electrode processes. As a rule, the same regularities are seen when the alloying additives are effective cathodes.

The corrosion resistance of most of the binary alloys is much lower than that of high-purity magnesium. Alloys with manganese, zirconium, cadmium, neodymium, lead and tin have higher corrosion

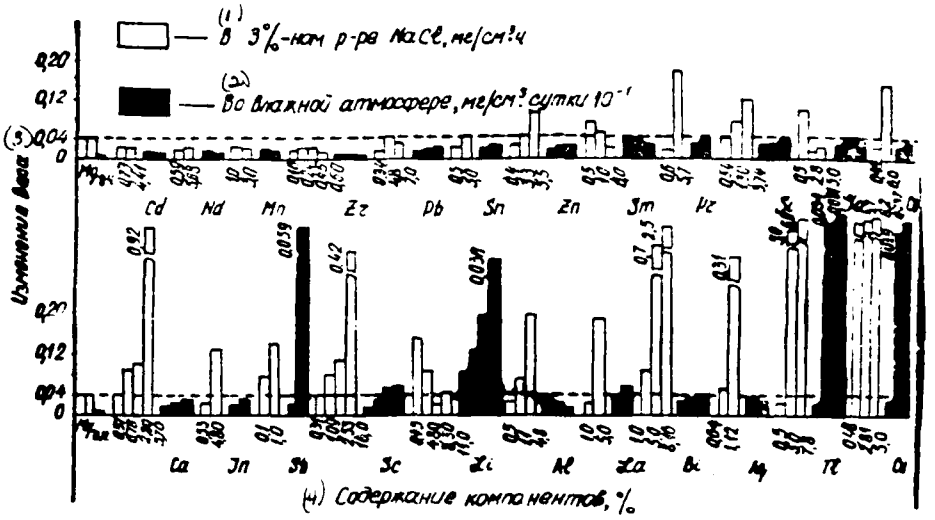

Fig. 1. Effect of alloying on corrosion resistance of magnesium in a 3% solution of NaCl and in a humid atmosphere.

KEY: (1) In a 3% solution of NaCl, mg/cm^3·h. (2) In a humid atmosphere, mg/cm^3·day 10^{-1}. (3) Change in weight. (4) Content of components, %.

resistance than magnesium with both small and large contents of the component. Alloys of magnesium with aluminum, indium, thallium, lanthanum, cerium and praseodymium have higher corrosion resistance than magnesium with small contents of the component, and alloys of magnesium with gallium and samarium - with high contents of the component (around 5%). Alloys of magnesium with copper, thallium (at high contents), silver, bismuth and antimony, and also alloys of magnesium with a high content or rare-earth metals and scandium have low corrosion resistance.

Almost all the investigated alloys, except for the alloys of the Mg-Li, Mg-Ga and Mg-Sm systems, have higher corrosion resistance at a content of the alloying component of up to 0.5% than the alloys

containing 5% or more of the component. This is obviously connected with the formation of homogeneous solid solutions at a low (up to 0.5%) content of the alloying component, or when the component has low solubility, with the insignificant amount of liberated cathode phases.

As the investigations showed, the potentials of the alloys are not the determining factor of corrosion resistance in magnesium alloys. However, if we know how the potential varies through time and with the percentage of the alloying component, we can determine and explain the nature of the corrosion process.

The data from the electrochemical measurements showed that the nature of the variation in the electrode potentials of the alloys through time and the stationary potential of magnesium differs depending on alloying.

A large number of the investigated elements have a detrimental effect on the stationary potential of magnesium to a greater or lesser extent (depending on the alloying metals). The metals Tl, Ga and Pb make the potential of pure magnesium significantly worse. The metals Sc, Ce, Ca, In, Nd and Pr do not make the potentials more than 50 mV worse. The stationary potential of magnesium is improved when it is alloyed with Cu, Bi, Sb, Al, Mn and Zn. The metals Sn, Cd, Li, Al, Si, La, Sm and Zr essentially do not affect the stationary potential of magnesium or the change the potential one way or the other by

less than 20 mV, i.e., by a value with falls within the limits of error of the experiment.

Because of the convergence of the curves, the variation in the potentials through time occurs selectively for some of the most typical binary alloys (Fig. 2). This graph also gives a diagram of the variation in the electrode potentials for all the investigated alloys in a 3% solution of NaCl.

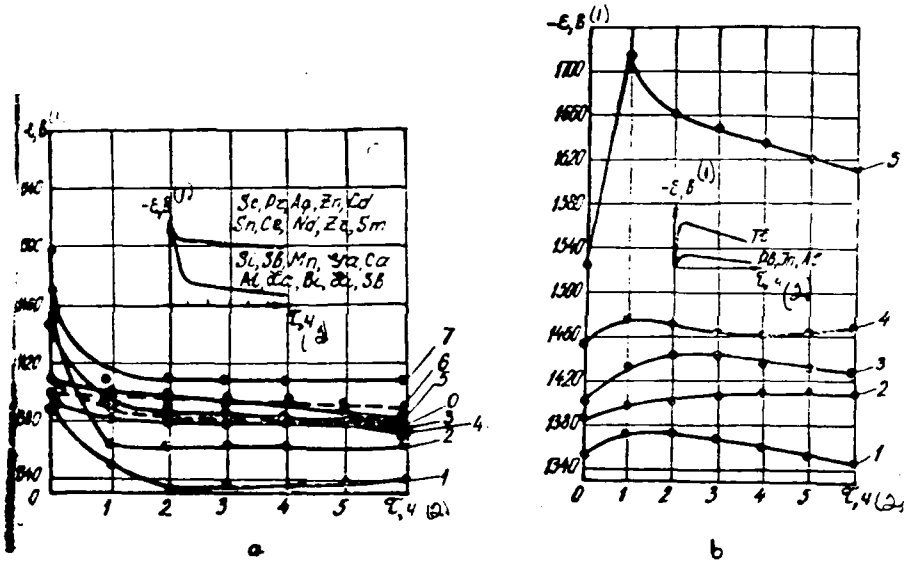

Fig. 2. Variation in potentials of high-purity binary magnesium alloys through time in a 3% solution of NaCl:

a) 0 - high-purity Mg; *1* — Mg — 8,1 Bi; *2* — Mg — 0,5 Al; *3* — Mg — 2,5 Sc; *4* — Mg — 1,0 Sb; *5* — Mg — 5,7 Pr; *6* — Mg — 5,4 Sm; *7* — Mg — 5,0 La;
b) *1* — Mg — 4,8 Al; *2* — Mg — 4,8 Pb; *3* — Mg — 4,8 In; *4* — Mg — 7,0 Pb; *5* — Mg — 10 Tl.

KEY: (1) V. (2) h.

The electrode potentials of the majority of binary alloys are regularly improved through time, obviously because of the corrosion

of magnesium alloys and the concentration of the alloying component on the surface [reference illegible][1]. The potentials of the most corrosion-resistant alloys, Mg-Zr, Mg-Nd and Mg-Cd, through time are insignificantly improved.

The improvement of the potential of alloy Mg-Li is obviously caused to a great extent by the selective dissolution of lithium, whose potential is more negative than that of magnesium. The curves of the variation in the potentials of alloys Mg-Tl, Mg-Pb, Mg-In and Mg-Al at a high content of the components also have their singularities. A natural film which is not sufficiently stable and which cannot prevent the intense corrosion of the alloy in a 3% solution of NaCl, but which has a significant effect on the potential of the alloy, forms on the surface of alloys Mg—5.0 Tl and Mg—8.0 Tl [?]. When the specimen is submerged in the solution, the film is destroyed and the potential becomes worse, after the corrosion of magnesium begins, thallium is concentrated on the surface, and the potential begins to improve again. The natural film is more stable on the alloy with a small thallium content, and the curve does not have a peak.

The curves for alloys Mg-Pb, Mg-Al and Mg-In, as well as for the alloys with a high thallium content have a peak, but one that is not as high.

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[1] See also Gratsianskiy, N. N. "Study of Corrosion and Electrochemical Behavior of Solid-Solution Alloys." Dissertation. Institute of General and Inorganic Chemistry of the Academy of Sciences UkrSSR, Kiev, 1960.

Thus, as their potentials vary through time, binary alloys can be divided into groups, which are schematically diagrammed in Fig. 2.

Conclusions

1. As a result of the systematic investigation carried out, the effect of 23 alloying components (Li, Cu, Ag, Ca, Zn, Cd, Al, Sc, Ga, In, Sm, Nd, La, Ce, Pr, Tl, Si, Zr, Sn, Pb, Sb, Bi, Mn) on the corrosion behavior of magnesium alloys in a 3% solution of NaCl and in a humid atmosphere was studied. The values of the stationary potentials and the variation in the potentials through time were determined.

2. It was established that the corrosion resistance of magnesium alloys is improved by the alloying components Zr, Mn, Cd, Nd, Sn and Pb within the limits of the investigation; Al, In, Tl, La, Ce and Pr - in a quantity up to 0.5%; and Ga and Sm - in a quantity of around 5%.

The corrosion resistance of magnesium alloys is lowered by the components Ag, Bi and Sb within the limits of the investigation; and the components Ce, La, Pr, Ca, Sc and Tl - in a quantity of 5% or more.

3. At a component content of up to 0.5%, the corrosion resistance of all the alloys, except for Mg-Li, Mg-Mn, Mg-Sm and Mg-Ga, is significantly higher than for the same alloys with a component content of 5% or more, whether or not the component forms a solid solution.

4. The corrosion rate of the alloys in a humid atmosphere is two orders of magnitude lower than in a 3% solution of NaCl.

5. The components which make the stationary potential of magnesium significantly worse are: Tl, Ga and Pb. The stationary potential of magnesium is improved by Cu, Al, Zn, Bi, Sb and Mn. The rest of the components investigated change the stationary potential of magnesium by 20-50 mV.

6. The electrode potentials of the majority of binary magnesium alloys regularly improve through time; alloys Mg-Tl, Mg-Al, Mg-In and Mg-Pb are the exception. Their potentials become worse.

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